

New Surface Allotropes of Carbon

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Abstract

The simplest negatively curved (schwartzene) surface allotrope of carbon, C_{32} -trousers, is introduced and modeled. Restricted Hartree-Fock calculations show that C_{32} -trousers is a stable unit and also demonstrate the viability of several related schwartzenes. In contrast to many schwartzene structures proposed earlier, C_{32} -trousers is a reasonable target for organic synthesis.

Familiar forms of pure carbon are the lattice allotrope, diamond, and the surface allotrope, graphite. Within the past decade, attention has focused on surface allotropes of carbon having positive curvature and spherical topology (fullerenes) with pentagonal rings, most notably C_{60} , buckminsterfullerene, which has been synthesized and studied^{1,2}. More recently, the class of surface allotropes has been enriched by consideration of cylindrical tubules³, as well as more speculative examples (the schwartzenes) with more complicated topology involving negative curvature, requiring many heptagonal rings of carbon⁴⁻⁹. In this paper we investigate the simplest fundamental building unit for schwartzene surface allotropes, C_{32} -trousers. An interesting molecule itself, C_{32} -trousers also may be used to join tubules into systems of “bucky-plumbing” or assembled into periodic schwartzite structures^{4,6,7} with high moduli of elasticity and low density.

We define a molecule to be a surface allotrope whenever one can find a smooth surface passing through all the atomic nuclei, such that the electron density decreases locally as one moves normal to this surface. This concept is implicit in much of the previous work on carbon allotropes. A carbon surface allotrope will necessarily have each atom bonded to 3 neighbors; however this local combinatorial requirement is not sufficient to characterize a surface allotrope. For example, the structure in Figure 3a

depicts an allotrope composed entirely of trivalent carbons that is not a surface allotrope.

An important topological invariant of a surface is its Euler number χ , which for a closed or periodic surface determines the topology. For example, $\chi = 2$ characterizes a sphere, while $\chi = 0$ for a torus or cylinder (which can be viewed as the plane with suitable doubly- or singly-periodic identifications). If such a surface is tessellated with a network of hexagons, pentagons and heptagons, then it has been noted⁵ the numbers p and h of pentagonal and heptagonal rings on the surface must satisfy the Euler relation $p - h = 6\chi$. The Gauss-Bonnet formula implies that the total curvature of the surface is $2\pi\chi$. Flat, doubly-periodic graphite can be viewed as an unwrapped torus, hence only hexagons are needed. Positively curved surface allotropes will have an excess of pentagons, while negatively curved allotropes have an excess of heptagons. Trousers (see Figure 1) are topologically the most basic negatively curved surface, with $\chi = -1$. Surfaces of every topological type (besides the plane, sphere or cylinder) can be built from trousers. It is possible to make a tessellation of a trousers surface with exactly 6 heptagons and no hexagons. The resulting surface allotrope (C_{26} -trousers) fails to satisfy the classical double-bonding rules, however, and does not appear to yield a stable molecule. The simplest stable trousers surface allotrope of carbon satisfying the classical rules of valence is C_{32} -trousers consisting of 6 heptagons and 3 hexagons.

Quantum mechanical modeling at the restricted Hartree Fock (RHF) level using the AM1 semiempirical molecular orbital (MO) method yields the symmetric molecule shown in Figure 2. Since we are not carrying out computations on infinite networks of carbons with periodic symmetry, we terminated all unfulfilled carbon valences with C-H bonds. For example, C_{32} -trousers is computed using a $C_{32}H_{12}$ molecule. The presence of these C-H bonds will be implicit in our discussions, so we shall refer to our surface allotropes as being molecules of general structure C_n .

Unconstrained RHF-AM1 MO computations readily optimized to the D_{3h} structure of C_{32} -trousers. Bond lengths, Mulliken bond orders, and some important bond angles obtained from the optimization are summarized in the Table. There was no distortion, as has been computed for some carbon clusters that have non-singlet ground states¹⁰. (As a test of the methodology, we also optimized the structure of C_{60} -buckminsterfullerene, by RHF-AM1 and found agreement with the structures previously computed by semiempirical MO methods¹⁰ and with the experimental structure. For our C_{60} -buckminsterfullerene structure, $r_{C-C} = 1.385$ and 1.464 Å, while the experimental values are estimated¹¹ to be 1.40 ± 0.015 and 1.45 ± 0.015 Å by solid state

^{13}C nuclear magnetic resonance spectroscopy.)

The atoms along the three-fold rotation axis of C_{32} -trousers, while nominally of sp^2 hybridization, are actually pyramidalized. The resultant $C_2C_1C_7$ angle is only 116.8° , and the plane tangent to C_1 and equidistant from carbons C_2, C_7 , and C_8 makes a pyramidalization angle of 15.4° . The central carbon C_1 is joined to the peripheral carbons by bonds of 1.46 \AA , which have RHF-AM1 bond orders of 1.22. These bonds are longer and weaker than the C=C bond of benzene, 1.395 \AA and a bond order of 1.42.

The C_4C_5 -bond and its five symmetry equivalents on the trousers periphery all have bond lengths of 1.35 \AA and bond orders of 1.91. These values are similar to the RHF-AM1 values for ethylene, 1.326 \AA and 2.00, respectively. Localization of bonding in these positions does not appear to be an artifact of the valence-terminating hydrogen atoms, since we find similar bond lengths in the extended structures¹² shown in Figure 3. For instance, in the RHF-AM1 optimized structure of C_{60} -trousers dimer, the central bond corresponding to the $C_4 = C_5$ bond in C_{32} -trousers has a bond length of 1.38 \AA and a bond order of 1.77.

The set of six equivalent transannular bonds ($C_3 - C_{\bar{3}}, \dots$) all have bond lengths of 1.40 \AA and bond orders of 1.58, and so are computationally similar to those of benzene, despite the pyramidalization of the sp^2 carbons involved. Molecules with similarly pyramidalized sp^2 carbons are well known¹³. For instance 9,9'-didehydrodianthracene is stable at room temperature¹⁴. The computed structural parameters for C_{32} -trousers are within normal limits for bonding of stable molecules. We therefore see no structural reason why materials containing C_{32} -trousers would not be viable, although they may be reactive or difficult to synthesize.

For example, C_{60} -trousers dimer (Figure 3b) and C_{56} -diamond trousers (3c) are the basic units for building doubly and triply periodic schwartzites respectively. Scuse-ria has suggested more elaborate D_{3h} schwartzenes as well as some with tetrahedral symmetry⁹. The simplest schwartzene unit with T_d symmetry is our C_{52} depicted in Figure 3e, comprising twelve heptagons only.

Because its relative simplicity (compared to earlier proposed structures^{4-10,15}) should compensate for its additional strain energy, C_{32} -trousers is a target for rational organic synthesis. In addition, schwartzites and tubule-containing surface allotropes based upon C_{32} -trousers may yet be discovered among the increasingly rich variety of carbon allotropes¹⁶.

Endnotes

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Table. RHF-AM1 bonding parameters^{*}.

<u>Compound</u>	<u>Parameter</u> [†]	<u>Value</u> [‡]	<u>Bond Order</u> [§]
$C_{32}H_{12}$	C_4C_5	1.349	1.91
	C_2C_3	1.455	0.98
	C_1C_2	1.460	1.22
	C_3C_3	1.401	1.58
	$C_2C_1C_7$	116.8°	
	$C_3C_2C_9$	106.8°	
	$C_2C_3C_3$	111.8°	
	$C_3C_4C_5$	113.4°	
C_{60}	$(C-C) r_1$	1.464	1.10
	$(C-C) r_2$	1.495	1.50
ethylene	$C=C$	1.327	2.00
benzene	$C-C$	1.395	1.42

^{*}Computations were carried out using the SPARTAN computational chemistry software package (Wavefunction Inc., Irvine, CA version 3.1) implemented on a Silicon Graphics Indigo R4000 workstation. Initial structures were optimized using the MM2 force field included in SPARTAN. [†]See the numbering scheme of Figure 2 for C_{32} trousers. [‡]Lengths in angstroms (Å), angles in degrees (°). [§]Mulliken RHF-AM1-SCF bond order. ^{||}Buckminsterfullerene.

Figure 1. Tessellated trousers surface.

Figure 2. Stereographic view of RHF-AM1 optimized C_{32} -trousers. Open circles represents hydrogens used to terminate the twelve unsatisfied valences of C_{32} . Visualizations of structures were carried out using the QUANTA 4.0 program (Molecular Simulations Inc., Burlington, MA).

Figure 3. Views of schwartzite units and partial structures. a) Lattice allotrope composed of trivalent carbons (stereo pair) b) C_{60} -trousers dimer, D_{2h} symmetry. c) C_{56} -diamond trousers, D_{2d} symmetry. d) C_{52} unit, T_d symmetry (stereo pair) e) Part of network containing C_{32} -trousers. f) C_{32} -trousers-based nanocog.